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NOTES

Solid-State Effects on Selenate Vibrations in Yttrium and Some Rare Earth Selenates

Introduction

During our investigations on rare earth selenates and selenate complexes of transition elements (*1*), it was noticed that Raman spectral studies were lacking on these systems. Hajek and co-workers (*2*) have recently reported the ir spectra of some rare earth selenates. The present communication reports the laser Raman spectra of yttrium, samarium, gadolinium, and dysprosium selenates. The "crystal field effects" observed on selenate vibrations are discussed.

Experimental

Selenates of yttrium, samarium, gadolinium, and dysprosium were prepared by dissolving the respective carbonates (99.9% purity, procured from M/s. Indian Rare Earths Ltd.) in a little excess of selenic acid (*3*). The clear solution thus obtained was initially concentrated on a water bath, and later allowed to crystallize slowly over phosphorus pentoxide in a desiccator protected from light. The dried crystals were taken up for subsequent studies. The water contents in these solids were estimated by thermogravimetric analysis (TGA).

The ir spectra were obtained on Unicam SP-1200 and Perkin–Elmer 621 spectrophotometers in nujol. The salient features of the ir spectra are given in Fig. 1. The observed bands for selenate groups are listed in Table I.

The laser Raman spectra of the solid samples were recorded on Jobin Yvon Raman spectrophotometer Model Ramanor HG 2S using He–Ne laser radiation at 632.8 nm for excitation. The salient features of the Raman spectra are given in Figs. 2 and 3 and the observed bands are listed in Table I along with the ir data.

Results and Discussion

Nature of Selenate Vibrations

An isolated selenate group has tetrahedral (T_d) symmetry and nine normal modes of vibration. The symmetric stretching mode $\nu_1(A_1)$ and doubly degenerate symmetric bending mode $\nu_2(E)$ are only Raman active. The asymmetric stretching mode $\nu_3(F_2)$ and the asymmetric bending mode $\nu_4(F_2)$ are both Raman and ir active.

It is of interest to note that the features observed in the ir spectra of yttrium, gadolinium, samarium, and dysprosium selenates (Fig. 1, Table I) are the same as those reported by Hajek and co-workers (*2*).

It is seen from the Raman spectra of the selenates that degenerate bands are split. Further, ν_1 and ν_2 are ir active. These spectral features arise due to the crystal field effects as explained below.

The environmental or crystal effect may conveniently be considered as being made up of two components, one static and the other dynamic. Several authors have discussed these effects on the vibrations of molecules and molecular ions (*4–7*). The two most frequently used approaches to this problem are the site group (*8*) and factor group (*9*) approximations. Ross (*10*) has explained these in fairly good detail in his recent text.

The rare earth selenates belong to the

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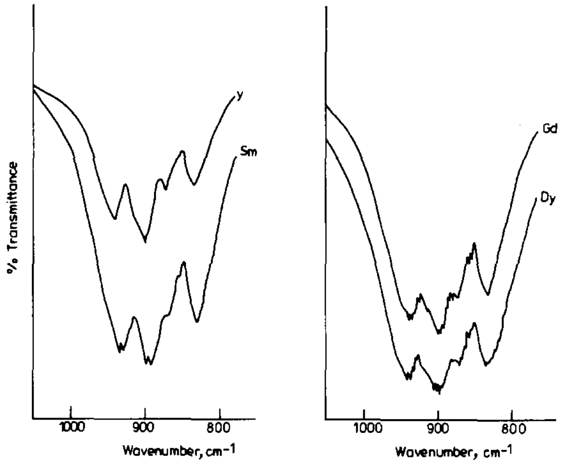

FIG. 1. Infrared spectra of yttrium, samarium, gadolinium, and dysprosium selenates in the region 750–1000 cm^{-1}.

space group C_{2h}^6–$C_{2/c}$ (centrosymmetric) or C_s^4–C_c (noncentrosymmetric) with $Z = 4$ (*2, 11*).

The selenate groups can occupy C_1 or C_2 sites in C_{2h}. Site C_i cannot be occupied as it is not a subgroup of T_d. For C_s^4 only C_1 sites can be occupied by selenates. Hence, the knowledge of the following correlations will

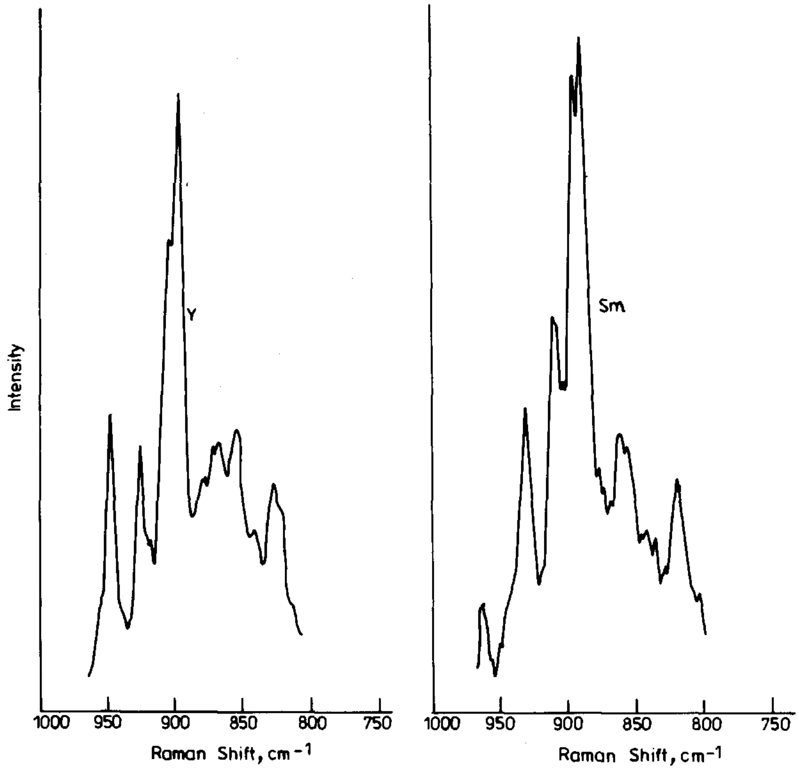

FIG. 2. Salient features of the laser Raman spectra of yttrium and samarium selenate.

TABLE I

THE ir AND RAMAN BANDS OF SELENATE VIBRATIONS

Name of compound	ν_1		ν_2		ν_3		ν_4	
	ir	Raman	ir	Raman	ir	Raman	ir	Raman
Yttrium		826		325		855		
selenate	835s		325sh		870s		350sh	350
$Y_2(SeO_4)_3 \cdot 7H_2O$		845		340		867		
						898		
					900s		375sh	378
						903		
						925		
					940s		400s	400
						948		
Samarium		820		323		865		
selenate	830s		320sh		865s		355sh	370
$Sm_2(SeO_4)_3 \cdot 6H_2O$		845		330		890		
						895		
					895s		375sh	375
						910		
						930		
					935s		400s	400
						960		
Gadolinium		820		290		855		
selenate	830s		330w		870s		350sh	350
$Gd_2(SeO_4)_3 \cdot 7H_2O$		840		305		862		
				325		895		
					895s		380sh	380
						900		
						920		
					935s		410s	410
						940		
Dysprosium		820		310		855		
selenate	830s		310w		870s		355sh	347
$Dy_2(SeO_4)_3 \cdot 3H_2O$		847		330		862		
						897		
					898s		380sh	382
						903		
						922		
					935s		405s	405
						944		

be of assistance in understanding the spectra.

Point group	Site group	Factor group
T_d	C_1, C_2	C_{2h}
T_d	C_1	C_s

Hajek and co-workers (*2*) have given an elaborate tabulation for these correlations. The same has been utilized in the interpretation of the Raman spectra of selenates.

In both ir and Raman spectra the static effect (site symmetry C_1) is clearly seen, but the dynamic effect (correlation splitting) is difficult to discern in the ir data. However, these two effects can be seen clearly in the Raman spectra (Figs. 2, 3, Table I).

In the centrosymmetric factor group C_{2h},

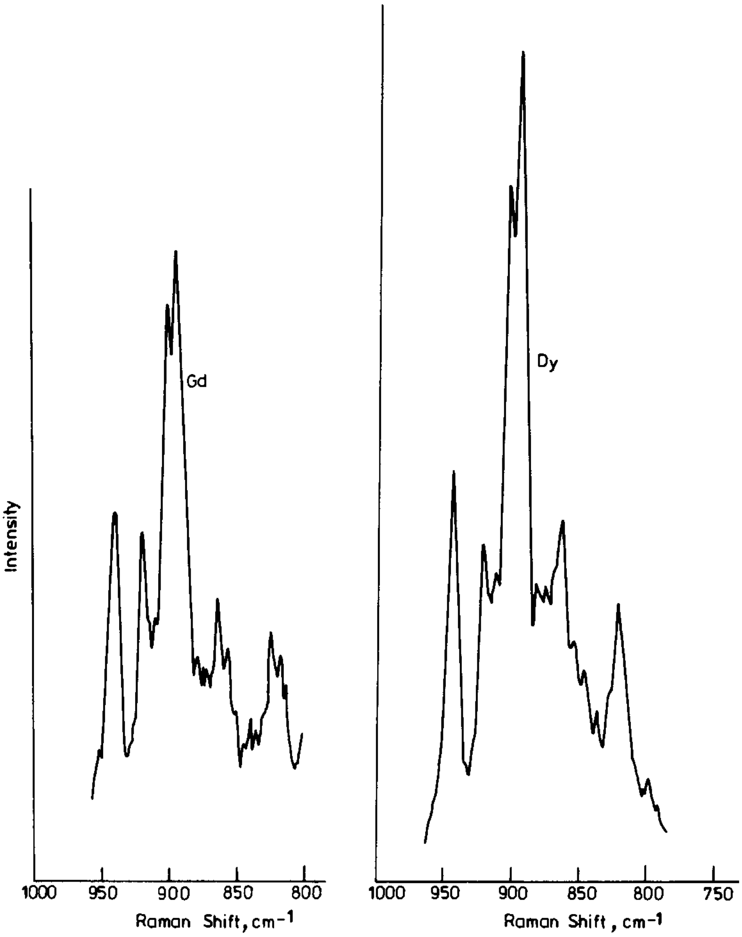

FIG. 3. Salient features of the laser Raman spectra of gadolinium and dysprosium selenate.

the "*u*" modes are ir active and the "*g*" modes are Raman active. Hence, in a crystal with $Z = 4$, we would expect six Raman bands each for ν_3 and ν_4, four bands for ν_2, and two bands for ν_1. Of these, the stretching mode ν_3 is of good diagnostic value.

It is seen from the Raman data given in Table I and Figs. 2 and 3 that ν_1 is split into two components $(A_g + B_g)$, as is clearly seen in the cases of gadolinium and yttrium. The bands are observed around 820 and 845 cm^{-1}. This band arises from a nondegenerate mode and its splitting has to be due to the dynamic effect only.

It is also of interest to note that the asymmetric stretching mode, ν_3, is neatly split into six bands, $3(A_g + B_g)$. These features are clearly seen from Figs. 2 and 3 in all the four cases. The bands are observed, for example, in the case of samarium selenate, at 865, 890, 895, 910, 930, and 960 cm^{-1}.

The bending modes ν_2 and ν_4 also show some splitting, but it is difficult to analyze the data because of the noise level in this region. Decius points out that ν_4 does not split much in all the tetrahedral ions (*5*). Khanna and Stranz (*12*) have also encountered this behavior.

It is thus seen that the static as well as dynamic effects are clearly encountered experimentally on the ν_3 mode in all the rare earth selenates reported in this paper. The asymmetric stretching mode (ν_3) therefore serves as a good diagnostic tool.

The ir bands arising due to water molecules are similar to those reported by Hajek and co-workers (*2*).

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References

1. M. K. Gupta and G. V. Jere, *Synth. React. Inorg. Met. Org. Chem.* **11,** 5 (1981).
2. B. Hajek, N. Novotna, and J. Hradilova, *J. Less-Common Met.* **66,** 121 (1979).
3. G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, p. 432, Academic Press, New York (1963).
4. W. C. Price, W. F. Shermon, and G. R. Wilkinson, *Proc. Roy. Soc. Ser. A* **255,** 5 (1960).
5. J. C. Decius, *J. Chem. Phys.* **49,** 1387 (1968).
6. S. S. Mitra, "Optical Properties of Solids," Plenum, New York (1968).
7. B. J. Berenblut and P. Dawson, *Spectrochim. Acta Part A* **31,** 1541 (1975).
8. R. S. Halford, *J. Chem. Phys.* **14,** 8 (1946).
9. S. Bhagavantam and T. Venkatarayudu, "Theory of Groups and Its Application to Physical Problems," 3rd ed., Andhra University, Waltair (1962).
10. S. D. Ross, "Inorganic Infrared and Raman Spectra," McGraw–Hill, New York (1972).
11. E. G. Sherry, *J. Solid State Chem.* **19,** 271 (1976).
12. R. K. Khanna and D. Stranz, *Spectrochim. Acta Part A* **36,** 387 (1980).

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